

Effect of spin rotation on the ${}^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum of Cr_2O_3 †

J. W. Allen

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 29 June 1973)

Experimental data showing how the positions, intensities, and polarizations of the ${}^4A_2 \rightarrow {}^2E$ optical exciton absorptions in Cr_2O_3 change as spin rotation occurs are presented. Differences between the data reported here and data reported previously by Stager are pointed out and discussed. A qualitative interpretation of the observed behavior is given and it is conjectured that most of the spin-rotation effects arise from changes in the role of spin-orbit coupling as the spins rotate. A change in the assignments of some of the exciton lines is suggested.

I. INTRODUCTION

Cr_2O_3 is a uniaxial antiferromagnet ($T_N = 308$ K). The optical-absorption spectrum of Cr_2O_3 displays, in the vicinity of 7000 Å, five reasonably sharp polarized absorption lines. These lines are associated with the ${}^4A_2 \rightarrow {}^2E$ transitions of the Cr^{3+} ions in the material, but display the effects of the formation of Frenkel excitons due to the transfer of optical excitation via inter-ion interactions. In particular, Allen *et al.*¹ have analyzed the separations in the spectrum as various exciton Davydov splittings. Additionally it is known that a magnetic field applied along the crystal c axis, and exceeding the critical value $H_c = 59$ kG, induces spin flop, in which the spins rotate to the basal plane. Thus Cr_2O_3 is an attractive material in which to study the effect of spin rotation on exciton Davydov splittings.

Recently data have been presented showing some of the effects on the Cr_2O_3 ${}^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum due to the application of a c -axis magnetic field exceeding the critical value H_c , required to induce spin flop.² In the same paper, data were also presented showing that uniaxial stress induces similar effects on the absorption spectrum, and this was interpreted as evidence that uniaxial stress induces spin flop in Cr_2O_3 . In a second paper³ the phenomenon of uniaxial-stress-induced spin flop in Cr_2O_3 was analyzed in detail. In neither of these papers were the optical data presented or discussed to an extent greater than was required to focus attention on the stress-induced spin flop. Also there is partial disagreement between the magnetic field behavior observed in the present experiments and that reported previously by Stager.⁴ This paper presents, in greater detail than before, the data showing how the positions, intensities, and polarizations of the optical absorptions change as the spins rotate, and gives a qualitative interpretation of the observed behavior, including why it differs from that reported by Stager.

The remainder of the paper is organized as follows: Sec. II discusses the experimental techniques

employed, Sec. III presents the magnetic field data, Sec. IV presents the uniaxial-stress data, and Sec. V gives a discussion of the data.

II. EXPERIMENTAL

Most of the samples used in these studies were cut from a flame-fusion-grown boule obtained from Lefever. Thin sections about 80 μ thick were obtained by cutting, grinding, and polishing. The use of thin sections is necessitated for absorption studies by the high background absorption in the wavelength region of interest. The samples were oriented so that the plane of the sample was normal to a crystal a axis and contained a crystal c axis. The sample areas were about 1 mm² for the stress studies and about 2 mm² for the magnetic field studies. One other sample used was obtained from Folweiler and consisted of a thin layer of Cr_2O_3 grown by vapor transport on a piece of crystalline sapphire 1 mm thick. The Cr_2O_3 was oriented with the crystal c axis normal to the thin layer. The sample was prepared by cutting out a piece 4 mm long and 1 mm wide, with the crystal a axis parallel to the long edge. This piece was used to obtain axially polarized stress data, as described below.

All the data were taken by passing the light from a water-cooled tungsten lamp through the sample and into a 1-m Czerny-Turner grating monochromator. For the slit widths and gratings employed, the spectral resolution was 0.8 cm⁻¹. Light from the monochromator was detected with a cooled S-20 photomultiplier and a current meter, with the current-meter reading displayed on a chart recorder. Linearly polarized spectra were obtained by placing pieces of Polaroid HN22 sheet polarizer between the sample and the monochromator.

The magnetic field data were obtained using a 100-kG superconducting magnet. The sample was mounted in a cold-finger liquid-helium Dewar whose tail section extended vertically downward into the magnet core and was equipped with a single sapphire window at the bottom. Light from the

tungsten lamp was passed upward from the bottom of the magnet core into the Dewar, through the sample, back down out of the magnet core, and into the monochromator with an arrangement of mirrors, as shown in Fig. 1. As shown in Fig. 1, the sample is mounted so that the magnetic field lies along the c axis and the light is incident normal to the plane of the sample. The sheet polaroid was placed immediately behind the sample inside the Dewar. The magnet was placed about 10 ft from the monochromator to avoid influence on the photomultiplier by the magnetic field. From the absorption line positions and previous data on the temperature dependence of the line positions,¹ the sample temperature is known to be less than 15 K.

Uniaxial stress was obtained from a commercial oil hydraulic piston mounted to press against a long stainless-steel rod that extended, inside a stainless-steel guide, downward into a liquid-helium-immersion Dewar. Because of the need for very thin samples in these experiments, the stress was applied to the sample's flat surfaces, and since the light must also be propagated normal to these surfaces, the arrangement shown in Fig. 2 was employed. The long rod presses against a sandwich consisting of a hollow stainless-steel piece with a lateral hole and a mirror inside, a copper pad with a small aperture, a crystalline-sapphire plunger, the sample, a crystalline-sapphire anvil, a second pad with aperture, and a second stainless-steel piece with mirror and hole. The sandwich rests against a screw in the bottom of the stainless-steel guide. The light is passed horizontally into and out of the lateral holes in the stainless-steel pieces,

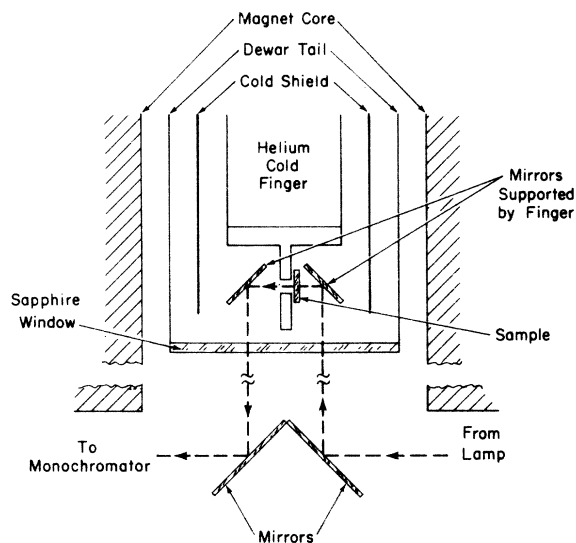


FIG. 1. Experimental arrangement for obtaining magnetic field data.

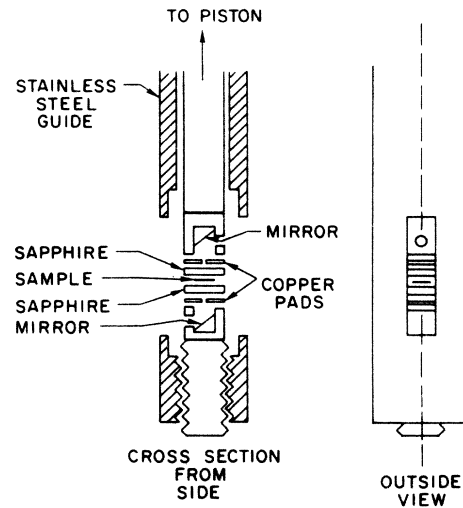


FIG. 2. Experimental arrangement for obtaining uniaxial-stress data.

and the mirrors in the pieces reflect the light vertically through the sandwich. The sapphire plunger and anvil act to deliver a reasonably uniform stress to the sample, although the data show evidence of some stress inhomogeneity, as discussed in Sec. IV. Optical alignment of the sandwich was accomplished with a small helium-neon laser and fixed with a very small applied stress prior to insertion of the stresser into the Dewar. The liquid helium in the sample chamber was pumped below the lambda point to avoid noise due to helium bubbles and to achieve a low temperature where the sample is most resistant to shattering from the applied stress.

For the sample consisting of a thin layer of Cr_2O_3 grown on sapphire, described above, the sandwich arrangement was not used. The sample was pressed on directly between the long rod and the bottom screw. The thin Cr_2O_3 was supported by its bond to the sapphire. Light was propagated normal to the sample surface, parallel to the crystal c axis, yielding an axially polarized spectrum. After two experiments, the Cr_2O_3 separated from the sapphire backing and the sample could no longer be used.

III. MAGNETIC FIELD DATA

The effect of a c -axis applied magnetic field on the positions of the strongest four of the five absorption lines mentioned in Sec. I was first studied and reported upon by Stager⁴ in 1963. Stager's data are shown on the left in Fig. 3, and the zero-field lines are labeled 1-4, in order of increasing energy. A weak higher-energy line, denoted here as 5, is not shown. In more recent low-field ($H < H_c$) studies of the four lines, van der Ziel⁵ showed that line 2 is split in zero field, but with absorp-

tion to one component becoming zero for zero field, and that line 3 is independent of field for $H < 50$ kG. The data obtained in the present study for the variation with field of all five of the lines are shown on the right in Fig. 3. It is evident that there is considerable difference between the two sets of data in Fig. 3, especially as regards the behavior of lines 3 and 4 in the spin-flop region. Other differences are the size of some of the splittings and the details of the way lines 1 and 2 approach one another for $H > H_c$.

An understanding of the origin of the differences in the two sets of data for lines 3 and 4 can be obtained by examining the intensities of lines 3, 4, and 5 as H increases through H_c . In the vicinity of the spin-flop region the intensity of line 5 rather suddenly increases until it is comparable to that of line 4, while the intensity of line 3 decreases rather abruptly and goes nearly to zero at high fields. These intensity changes can be seen in the traces of Fig. 4, which also shows polarization effects that will be mentioned below. It is proposed here that Stager did not observe lines 3 and 5 for the values of field where their intensities are small and hence was forced to connect his experimental points in the spin-flop region, as he did. With this possibility in mind, an examination of the two sets of data shows that the actual data points are largely in accord with one another.

Thus in the present study, the position of line 3

is found to be independent of the field strength, while line 5 has a behavior similar to that of line 2. In the low-field region, lines 1 and 4 split and lines 2' and 5' appear and separate from lines 2 and 5. As the field increases through H_c , these effects tend to disappear and, by pairs, the positions of lines 1-2 and lines 4-5 become nearly coincident.

As Fig. 4 shows, the intensity changes that occur in the spin-flop region are polarization dependent. With zero magnetic field, lines 1 and 4 are σ and axially polarized, lines 2 and 3 are π polarized, and line 5 is σ and π polarized. In the spin-flop region the intensity of line 5 increases in σ and axial, but not π , polarization, the intensity of line 3 first increases in σ and axial polarization and then goes nearly to zero in all polarizations, and the intensity of line 2 increases in σ and axial polarization to become as large as that of line 1. The conditions under which the data were taken did not permit accurate numerical measurement of the line intensities, but qualitatively there does not appear to be a conservation-of-intensity law acting among any of the lines as their intensities change. It should be pointed out here that axially polarized data were not readily obtainable with the geometry imposed by the magnet. The axial-polarization effects just described were actually observed in the stress experiments, described in Sec. IV: since the σ - and π -polarization effects are identical for

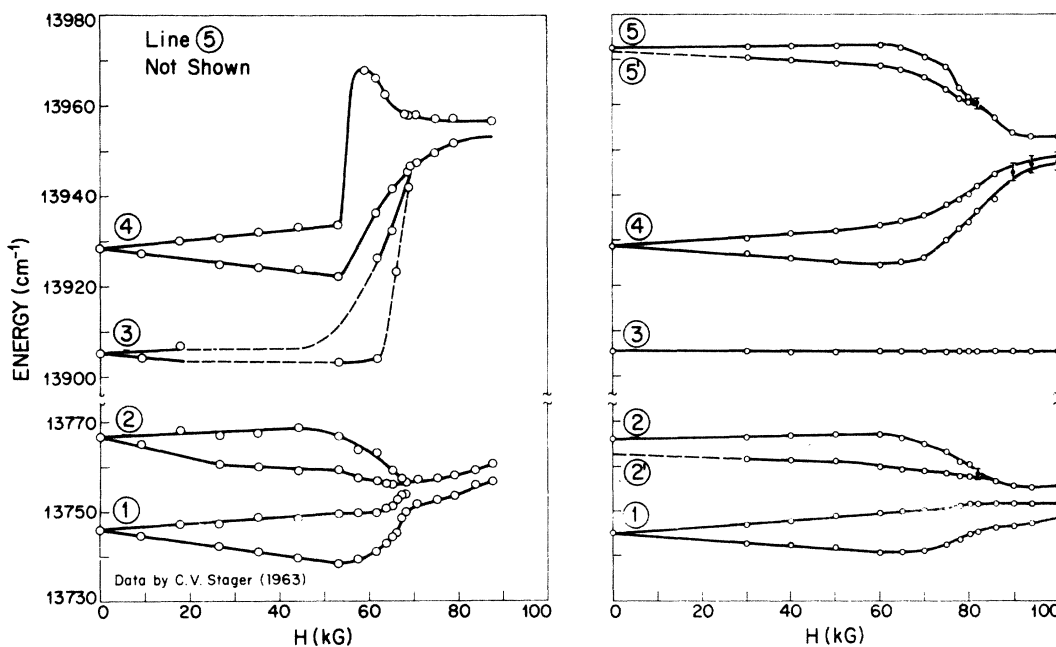


FIG. 3. Variation of exciton line positions with c -axis magnetic field strength as determined in present experiment and by C. V. Stager [J. Appl. Phys. 34, 1232 (1963)].

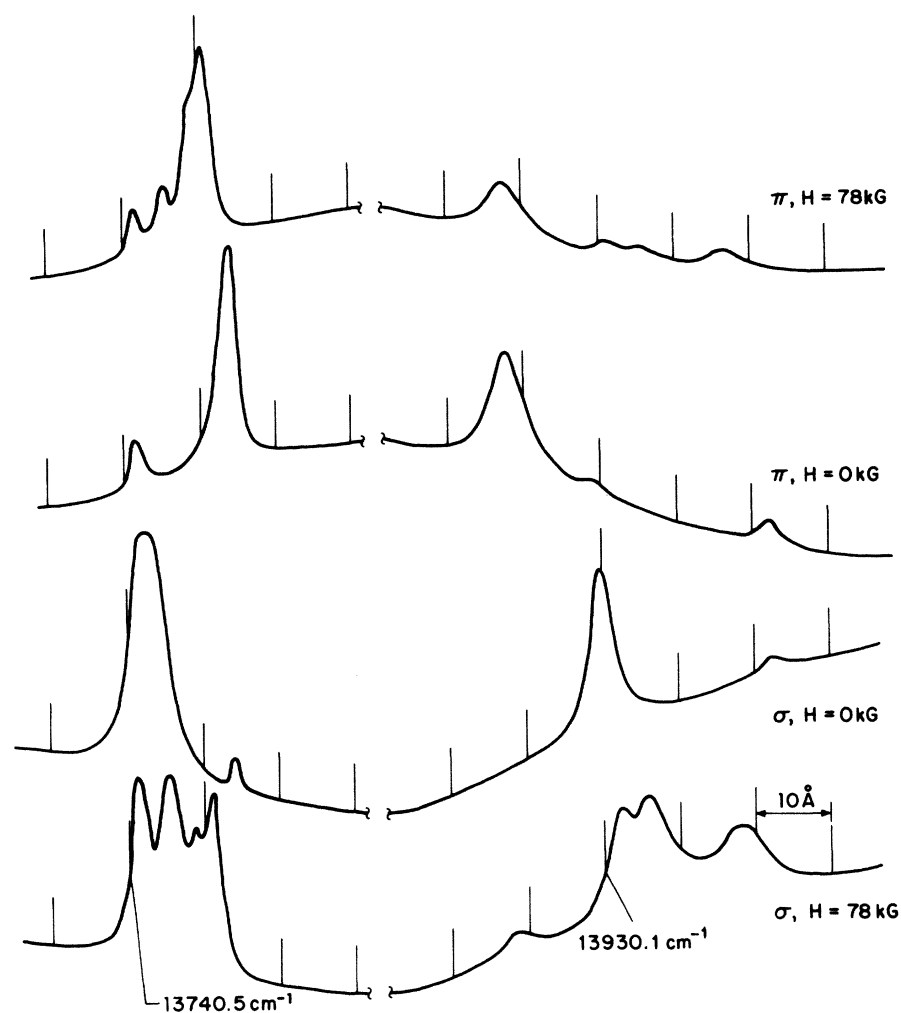


FIG. 4. Polarized data traces for magnetic field strengths of 0 and 78 kG.

the magnetic and stress data, it is reasonable to believe that axially polarized magnetic field data would yield no additional information. Above, for the sake of clarity, all the polarization effects believed to occur as the spins rotate were described together.

As mentioned above, there are some other more-minor differences between the two sets of data in Fig. 3 than the ones already discussed. In particular, in the present data the low-field-region splittings are smaller for a given field strength, and the point where the splittings are nearly gone occurs at a higher-field strength. It is proposed here that this is because of small differences in the alignment of the field with the crystal c axis in the two experiments. Both sets of data show evidence of misalignment of the magnetic field and the c axis in that the spectrum does not change discontinuously at the spin-flop field. It is known⁶ that any misalignment causes the spins to reorient gradually, and that as much as 5° misalignment smears out

the transition, so it occurs from about $0.6H_c$ to $1.4H_c$, with the full perpendicular alignment of the spins with the c axis only being approached for the field many times larger than H_c .

To test this hypothesis, the sample c axis was deliberately misaligned with the field by about 30° . The variation of the line positions with field strength for this situation is shown in Fig. 5. The low-field splittings are even smaller than in the data of Fig. 3, and the splittings do not disappear even at 100 kG. The direction of the differences in the data of Figs. 3 and 5 supports the hypothesis that in Stager's experiment the alignment of magnetic field and c axis was better than in the present experiment. It was also observed that in the misaligned case, the intensity changes in lines 3 and 5 were much more gradual than in the better aligned case, lending support to the earlier proposal that in Stager's experiment, where the alignment was probably quite good, these effects were very abrupt and went unnoticed. It appears that there is, in fact,

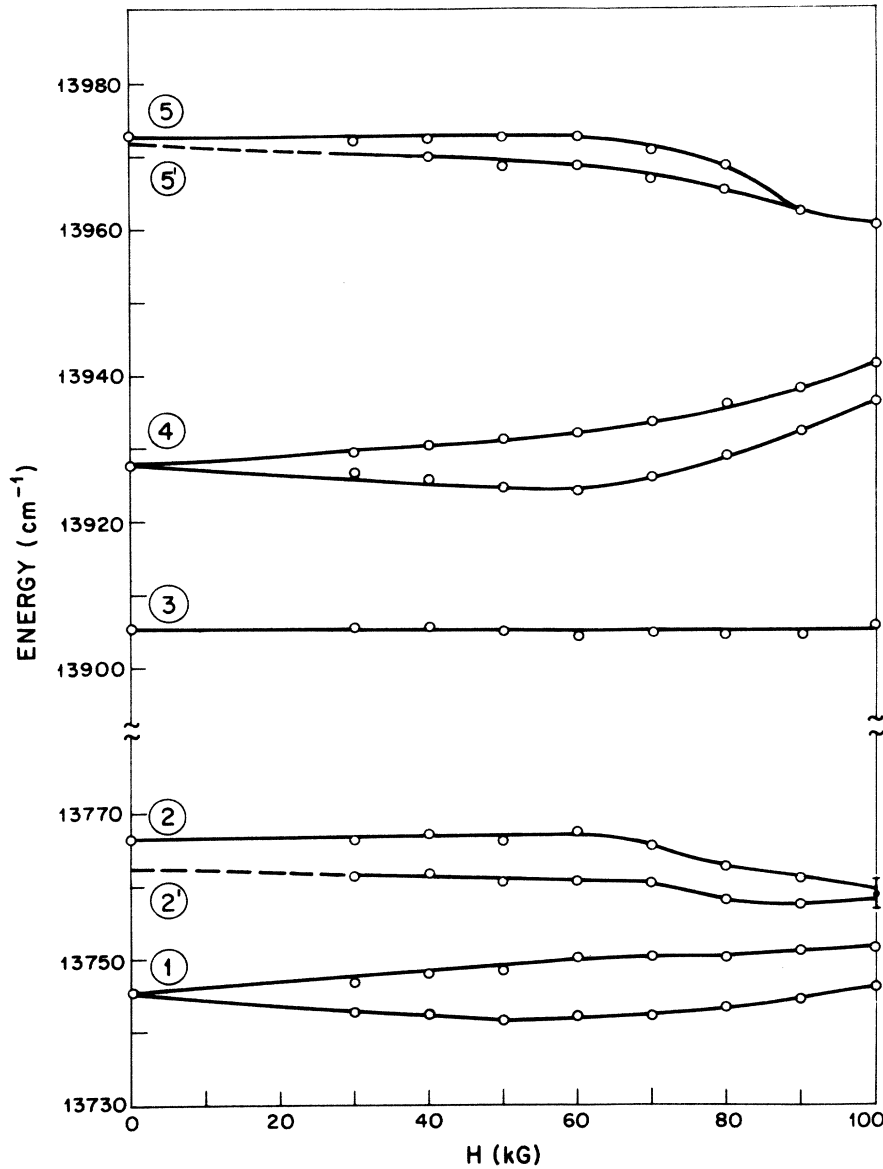


FIG. 5. Variation of exciton line positions with strength of magnetic field applied about 30° away from crystal c axis.

some advantage to a slight misalignment in that it is much easier to observe the changes taking place. For example, in the present data it is clear that lines which split out from one another in pairs are returning to each other in pairs, and this was not entirely clear in Stager's data.

IV. UNIAXIAL STRESS DATA

The effect of uniaxial a -axis stress on the positions of the five lines is shown in Fig. 6, along with the magnetic field data for comparison. For small values of stress the lines shift linearly and nearly uniformly to lower energies, with no changes in intensity or polarization. As the stress is increased through 15 kbar, by pairs the positions of lines 1-2 and 4-5 become nearly coincident, as

occurs in the magnetic field data in the spin-flop region. The position of line 3 suffers a small anomalous departure from linear shifting and there is a hint that this effect is also occurring in the movements of the other lines. The position changes occurring in the vicinity of 15 kilobars are accompanied by polarization and intensity changes. For σ and π polarization these changes are identical to those described in Sec. III for the magnetic field data in the spin-flop region. The changes observed in axial polarization were also described in Sec. III, for completeness of presentation, even though there are no magnetic field data with which to compare them. It is reasonable to suppose that if the axial-polarization magnetic field data were available, it would be identical to the stress data. Fig-

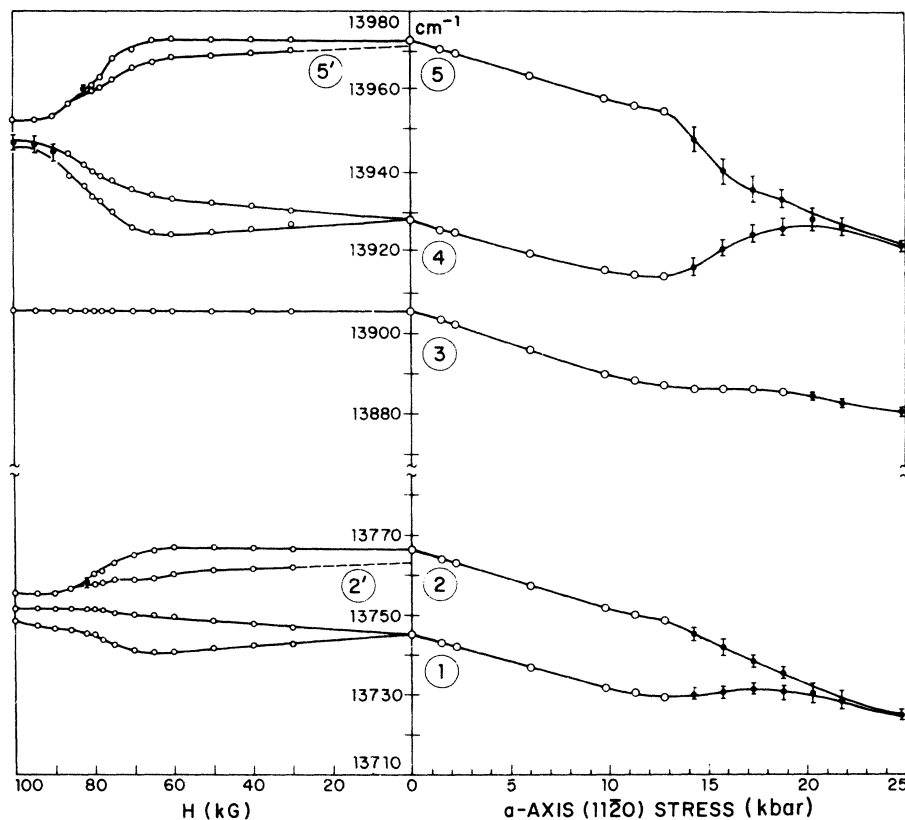


FIG. 6. Variation of line positions with magnitudes of applied c -axis magnetic field and a -axis uniaxial stress. For comments on the meaning of large error bars, see text.

ure 7 shows unpolarized data traces comparing the spectra for 20 kbar of stress, for 100 kG of field, and for no stress or field. As can be seen, the data for high stress and field are remarkably similar.

Figure 7 also shows that the quality of the stress data is not as good as that of the magnetic field data with respect to linewidths. This is undoubtedly due to inhomogeneities in the stress applied to the sample. The observation of gradual, rather than abrupt, changes in the spectrum is also due in part to stress inhomogeneities, although the detailed analysis of stress-induced spin flop showed that it is theoretically possible for the spins to rotate smoothly, rather than abruptly, to the basal plane. As pointed out previously,² the stress broadens the lines by about 5 cm^{-1} ; from the observed linear shifts of the lines, this implies a stress distribution of about 4 kbar. In the transition region, where the line positions are very stress sensitive, the lines become quite broad, some with asymmetric line shapes, which is the meaning of the large error bars in Fig. 6.

V. QUALITATIVE INTERPRETATION OF DATA

A quantitative analysis of the data presented above has not been made. However, a number of qualitative observations can usefully be made, and this is the purpose of this section. The effects of

principal interest here are those due to the rotation of the spins from the c axis to the basal plane as the applied magnetic field or uniaxial stress becomes large enough to induce the spins to rotate. The spectral changes arising for the magnetic field less than H_c have been analyzed in a previous paper.¹ The linear line-position shifts observed for low stresses are probably due to the effect of the hydrostatic component of induced strain, which varies the crystal-field parameters and inter-ion interactions that govern the single-ion splittings and exciton Davydov splittings.

The dominant feature of the line-position data of Fig. 6 is that as the spins rotate, lines 1-2 and 4-5 merge by pairs, while line 3 is substantially unaffected. The merging is not complete in the magnetic field data, but it is reasonable to ascribe this to incomplete rotation of the spins due to misalignment of the field with the c axis, as discussed in Sec. III. This behavior has two implications. The first involves a possible change in the line assignments of Allen *et al.*,¹ which will now be reviewed briefly.

The lines have been ascribed to absorption by $k=0$ Davydov split excitons arising from transitions of the Cr^{3+} ions from the lowest energy spin state of the exchange-split 4A_2 ground state to the two-lowest energy states of the exchange-split 2E state.

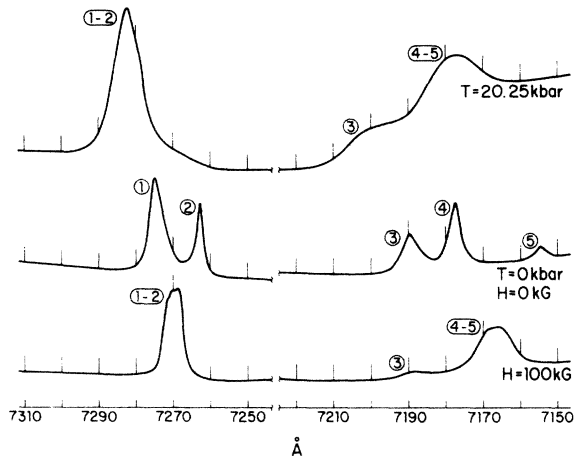


FIG. 7. Unpolarized data traces for zero magnetic field and stress, 20.25-kbar a -axis stress, and 100-kG c -axis magnetic field strength.

Because Cr_2O_3 has four ions per unit cell, there are four exciton states for each transition. A group-theory analysis shows that one transition gives rise to two (doubly degenerate) E excitons, and the other transition gives rise to two A_1 and two A_2 excitons, all nondegenerate. The symmetry labels refer to representations of the unitary subgroup D_3 of the magnetic factor group D_{3d} (D_3). From symmetry arguments it can be shown that electric dipole absorption is forbidden for the A_1 excitons, is allowed in σ and axial polarization for the E excitons, and is allowed in π polarization for the A_2 excitons. For magnetic dipole absorption, the A_1 excitons are forbidden, the E excitons are π and axially polarized, and the A_2 excitons are σ polarized. It can also be shown that an axial magnetic field splits the E excitons and couples the A_1 and A_2 excitons, permitting absorption by the A_1 excitons.

In assigning the observed lines to particular exciton states, Allen *et al.* followed the generally valid premise that when electric dipole absorptions are allowed, the electric dipole selection rules will dominate because electric dipole absorption is expected to be much stronger than magnetic dipole absorption. For zero field or stress, lines 1–4 are the strongest and their polarizations are consistent with the electric dipole selection rules if lines 1 and 4 are assigned as the two E excitons, and lines 2 and 3 are assigned as the two A_2 excitons. The behavior of the lines when a small axial magnetic field is applied is consistent with these assignments and the additional one that 2' is one of the A_1 excitons. It was assumed by Allen *et al.* that the other A_1 exciton was not observed because it was separated in energy too far from either of the A_2 lines to be coupled strongly to them by the

applied field. Because line 5 is much weaker than the others for zero field or stress, and does not obey the electric dipole selection rules for any of the excitons, it was regarded by Allen *et al.* as an "extra" line, not one of the excitons. They suggested that it was probably due to a double excitation process, such as magnon-exciton, which could have less restrictive selection rules.

Because line 5 participates in the general pattern of behavior of lines 1, 2, and 4, while line 3 does not, it is difficult to avoid the possibility that lines 5–5' are an A_2 – A_1 exciton pair and that line 3 has some other origin not presently understood. As mentioned above, the principal difficulty with this assignment of line 5 is that it does not obey the electric dipole absorption rules for an A_2 exciton in that it is observed in σ and π , but not axial, polarization. There are two possible explanations for this. First, the σ intensity may be due to incomplete polarization of the light because of c -axis wander in the crystal, misalignment of the polarizer with the c axis, or light propagation not normal to the c axis. If this explanation is right, the other four lines would be expected to show similar effects and, indeed, the data of Fig. 4 show intensity of comparable strength in electric-dipole-forbidden polarizations of the other four lines. But the fact that for line 5 the intensities in allowed and forbidden polarizations are comparable, while for the other four lines the intensities in allowed polarizations are much larger than in forbidden polarizations, makes this explanation unattractive. Also, in some samples, the intensity in forbidden polarizations is nearly zero for lines 1–4, while still present for line 5, and in axial polarization forbidden lines never occur. A second possibility is that the intensity in forbidden polarizations is due to magnetic dipole transitions. In fact, the observed polarizations of all lines are in strict accord with the group-theory selection rules if this possibility is admitted. However, the forbidden intensities are much stronger than would be expected for magnetic dipole transitions, and it is again difficult to understand why in some samples the forbidden intensity is nearly gone for line 1–4 while still present for line 5. Thus neither explanation is very palatable, and until a better one is found the polarization of lines 5–5' remains a barrier to their assignment as an A_2 – A_1 exciton pair.

However, since the other excitons are not entirely free of intensity in forbidden polarization, and since the strict selection rules, including the possibility of unusually strong magnetic dipole absorption, are not violated, it seems to the author that it is even less attractive to ignore the similarity of the behavior of lines 5–5' to that of the other excitons in the data of Fig. 6. The similarity to lines 2–2' could perhaps be understood if lines 5–5'

were some sort of double excitation involving lines 2-2', but this would not explain why line 4 should move toward lines 5-5'. Thus, it is tentatively proposed here, and assumed in the following discussion, that lines 5-5' are an A_2 - A_1 exciton pair and line 3 is an "extra" line of unknown origin. In the following discussion it will be shown that this reassignment permits a simple qualitative interpretation of the position shifts of lines 1, 2, 4, and 5.

The second implication of the merging of lines 1-2 with 4-5 with spin rotation concerns the effect of spin rotation on the transfer-of-excitation (TOE) matrix elements responsible for the exciton Davydov splittings and on the single-ion splitting of the 2E state by the spin-orbit interaction, the trigonal crystal field, and the exchange field. A symmetry analysis shows that for the A_1 and A_2 excitons there are three TOE parameters, denoted by Allen *et al.*¹ as H_{12} , H_{13} , and H_{14} , while for the E excitons there is but one parameter, $H_{13}(E)$. For both sets of excitons, the H_{13} parameters characterize TOE between same-spin sublattices and are quite large. The H_{12} and H_{14} parameters characterize TOE between opposite-spin sublattices and are much smaller. The symmetry analysis shows that if H_{12} and H_{14} were zero, the A_1 - A_2 excitons would occur as two degenerate pairs of states, with each pair consisting of an A_1 and an A_2 excitation, and the pairs separated by $2|H_{13}|$. The zero-field zero-stress lines, with the new assignments proposed above, and to a less extent with the old ones of Allen *et al.*, very nearly have this pattern. The final two elements entering the exciton splitting patterns are the splitting of the 2E state due to the spin-orbit interaction and the trigonal crystal field, and the possible difference in exchange splittings of the $\pm \frac{1}{2}$ spin components for the two orbital components of the 2E manifold. Both these effects displace the centers of gravity of the Davydov splitting patterns of the two sets of excitons, and would be the only source of splitting if all the TOE parameters were zero.

Phenomenologically, the merging of lines 1-2 and 4-5, with the new assignments proposed above, can be described by saying that after the spins have rotated, the parameters H_{12} and H_{14} are very small or zero, the parameters H_{13} and $H_{13}(E)$ are equal, the trigonal-field spin-orbit splitting of the 2E state is small or zero, and the exchange splittings for the two orbital components of the 2E state are equal. Under these conditions, the exciton splittings would be what are observed, two sets of four degenerate lines separated by a single parameter, $2|H_{13}|$.

All the effects just pointed out have a probable common origin—the effect of spin rotation on the spin-orbit interaction. Allen *et al.*² have made a de-

tailed microscopic analysis of the inter-ion exchange interactions and found that in the absence of spin-orbit coupling effects on the single-ion states, the TOE parameters H_{12} and H_{14} would be zero, that $|H_{13}| = |H_{13}(E)|$, and that the exchange splittings for the two orbital components of the 2E state would be the same. Of course, with no spin-orbit interaction, the spin-orbit trigonal-field splitting of the 2E state is also zero. Thus a possible conclusion is that spin rotation drastically reduces the effect of spin-orbit coupling on the various processes determining the exciton splitting pattern. In assessing this possibility it should be remembered that to the extent that the exchange field acts only on spin components of states, it tends to make pure-spin states within a manifold energetically favorable. This is especially the case when the exchange field does not point along the c axis of a uniaxial system. Evidently these ideas can be subjected to a theoretical test, and until this is done they must be regarded only as conjectures. A partially successful analysis of this type has been made in connection with changes observed in the absorption spectrum of MnF_2 as spin flop occurs.⁷

A somewhat less striking aspect of the line position data of Fig. 6 is that as spin rotation occurs, the splittings induced by the small magnetic field go to zero or nearly to zero. That all the splittings do not go completely to zero is again reasonably ascribed to incomplete rotation of the spins due to misalignment of the field with the c axis, as is discussed in Sec. III. Allen *et al.*² obtained a good description of the low-field splittings using Stager's model³ in which the axial magnetic field was superposed with the axial exchange field to increase the single-ion exchange splittings of the down-spin ions and decrease those of the up-spin ions. With this model, it would be expected that when the spins rotate so that all are perpendicular to the field, the magnetic splittings will go to zero because the magnetic field will affect all the ions equivalently. If the suggestion above, that spin rotation affects the role of the spin-orbit interaction, is correct, a detailed theory of the variation of the magnetic field splittings with spin rotation must also take into account the possibility of changes in the single-ion g values, since their departures from 2 involve the effects of spin-orbit coupling. Again, these ideas should be subjected to a theoretical test.

The intensity and polarization changes observed as spin rotation occurs can be summarized by saying that lines which are weak or absent in σ and axial polarization for zero field or stress acquire considerable intensity in σ and axial polarization, and line 3 ultimately loses almost all its intensity. The origin of the intensity of Frenkel excitons is generally presumed to be the intensity of the single-ion transition giving rise to the excitons, with

the distribution of intensity into the various Davydov components being governed by the amplitude and phases of the TOE matrix elements. Since there does not appear to be conservation of intensity among the Davydov components as the intensity changes occur, it is probable that the intensity changes are due to single-ion effects. The intensity of the ${}^4A_2 \rightarrow {}^2E$ transitions of the Cr^{3+} ion depend on, among other things, spin-orbit mixing of other spin-quartet states with the 2E states to circumvent the transition being spin forbidden. This suggests that an analysis of the effects of spin rotation on the role of the spin-orbit interaction may also provide an explanation of the observed intensity changes. An analysis of this type has been

made by Sugano *et al.*⁸ for the intensity changes observed in the ${}^4A_2 \rightarrow {}^2E$ excitons of YCrO_3 as spin rotation occurs. The loss of intensity in line 3 will not be explainable until an assignment for this line can be found.

In summary, the principal result of the discussion of this section is the conjecture that most of the spin-rotation effects arise from changes in the role of spin-orbit coupling as the spins rotate, and that an interchange of the previous assignments of lines 3 and 5 may be necessary.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the expert and creative technical assistance of L. G. B. Yee.

¹Work sponsored by the U.S. Air Force.

¹J. W. Allen, R. M. Macfarlane, and R. L. White, *Phys. Rev.* **179**, 523 (1969).

²J. W. Allen, *Phys. Rev. Lett.* **27**, 1526 (1971).

³J. W. Allen, *Phys. Rev. B* **7**, 4915 (1973).

⁴C. V. Stager, *J. Appl. Phys.* **34**, 1232 (1963).

⁵J. P. van der Ziel, *Phys. Rev.* **161**, 483 (1967).

⁶S. Foner, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I.

⁷R. S. Meltzer and L. L. Lohr, Jr., *J. Chem. Phys.* **49**, 541 (1968).

⁸S. Sugano, K. Aoyagi, and K. Tsushima, *J. Phys. Soc. Jap.* **31**, 706 (1971).